



Modulating the Structures and Physical Properties in Naphthalenediimide-Based Porous Molecular Conductors

著者	Qu Liyuan
number	86
学位授与機関	Tohoku University
学位授与番号	理博第3235号
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論文内容要旨

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氏 名	Liyuan Qu	提出年	令和元年
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Appendix

This study has demonstrated that the electrochemical method is a promising approach for the syntheses of electrically conductive porous coordination polymers (PCPs). This study focused on radical containing conductive PCPs that are constructed from redox-active molecule NDI via using electrochemical reduction. These conductive PCPs were named as porous molecular conductors (PMCs). The structural and physical properties of these as-synthesized frameworks were further modulated by external stimuli, such as solvation/desolvation and insertion of guest molecules.

Chapter 1 briefly introduced the development of PCPs and those studies related to host-guest interactions.

Chapter 2 shortly presented the NDI-based radical salts. The NDI ligand was reduced to $\text{NDI}^{\bullet-}$ at cathode and assembled to dark brown single crystals with diverse periodicities but without containing any metal ions inside. These crystals have high quality and possess high electrical conductivities up to $10^{-3} \text{ S cm}^{-1}$.

Chapter 3 described the physical properties and modulation of conductivities in **PMC-M(NO₃)₂** (M = Cd, Zn, Co and Ni). They are isostructural frameworks consisting of infinite 1D linear chain. Approximately 70% of NDI cores in those PMCs were reduced to $\text{NDI}^{\bullet-}$ species and 30% remained neutral according to their chemical formula. Indeed, a broad absorption band in visible region and sharp signal from EPR confirmed the existence of $\text{NDI}^{\bullet-}$. Furthermore, the C=C stretching appeared in both neutral and anionic regions, indicating that the coexistence of $\text{NDI}^{\bullet-}$ and NDI^0 . The intervalence charge transfer (IVCT) band of $\text{NDI}^{\bullet-}/\text{NDI}^0$ was detected in IR region with a top at 0.3 eV, leading to high conductivities up to $10^{-3} \text{ S cm}^{-1}$ (single crystals). The neutral NDIs in these PMCs afford redox activities to the frameworks. Moreover, their structures and conductivities were modulated by solvation/desolvation in a range of 10^{-8} – $10^{-2} \text{ S cm}^{-1}$. Either heating the single crystals at 210 °C or immersing crystals in organic solvent provide the desolvated species which show conductivity of $10^{-2} \text{ S cm}^{-1}$ in pressed pellets (10^4 times higher than as-synthesized). Exposure the desolvated sample into DMA vapor leads to a decrease of conductivity down to $10^{-8} \text{ S cm}^{-1}$. The tunability of the conductivity corresponds to the structural flexibility of linear chains PMCs.

Chapter 4 demonstrated the charge orders occurred in these infinite 1D π -stacked columns and thus prevented metallic conductions. **PMC-ZnX₂** (X = Cl, Br and I) consist of 1D linear and zigzag chains with the ratio of 1:2. The charge of NDI was directly calculated from chemical formula to be -0.7 . The coexistence of $\text{NDI}^{\bullet-}$ and NDI^0 was confirmed by combining UV-Vis, IR and EPR spectroscopies. The charge of NDIs was calculated by the equation summarized by our group. The results of the calculation also proved the evidence of charge orders occurred in these PMCs. Moreover, the metal nodes can be removed by 2,2'-bipyridine in the solution of toluene, indicating that **PMC-ZnX₂** have large pores and their structural flexibility.

Chapter 5 shortly introduced the structures and conductivities of 2D sheets frameworks **PMC-CdBr₂** and **PMC-PdBr₂**. The conductivity of **PMC-CdBr₂** was measured to 1.2×10^{-2} S/cm in single crystal, which is one of the highest values among all the PMCs.

Chapter 6 illustrated two polymorphic frameworks presenting 2D and 3D structures. They have very robust single crystals than other 1D PMCs. Using SO_4^{2-} as pillaring ligand, the dimensionality of PMCs was successfully increased to 2D and 3D, provided large robust crystals which are very convenient for physical property measurement. The 2D framework **PMC-ZnSO₄-2D** shows one of the highest conductivities among all the PMCs (10^{-2} S/cm). This study demonstrated that using co-ligand for the syntheses of PMCs is feasible.

論文審査の結果の要旨

一次元電子系物質は、様々な電子状態が安定に存在し得ることから、外場応答性を有する機能性物質として有望である。しかしながら、分子吸脱着といった化学的刺激に応答する一次元電子系物質は極めて稀であり、有効な合成戦略も存在しなかった。瞿李元氏は、有機合成により構造の微細なチューニングが可能な分子性導体に着目し、多孔性配位高分子 (MOF) と融合することで、両者の特長を併せ持つ多孔性分子導体 (Porous Molecular Conductor; PMC) を開発することを目的として研究を行った。

瞿李元氏は、広い π 共役平面と低い LUMO エネルギーを有し、アニオンラジカル状態が比較的安定なナフタレンジイミド (NDI) に 2 つのピリジル基を導入することで架橋配位子 NDI-py を合成した。この NDI-py からなる分子性導体を定電流電解によって合成した (2 章)。また、種々の金属イオン存在下で定電流電解を行うことで、直線状一次元配位高分子が π 積層した PMC (3 章)、直線状一次元配位高分子とジグザグ状一次元配位高分子が 1:2 の比で集積した PMC (4 章)、二次元配位高分子が π 積層した PMC (5 章)、硫酸イオンが架橋配位子として作用した二次元及び三次元配位高分子からなる PMC (6 章) をそれぞれ合成した。このように瞿李元氏は、電解法により導電性と多孔性を併せ持つ新奇な物質系の開発に成功した。

3 章で合成した PMC-Cd(NO₃)₂ は、結晶溶媒である N,N-ジメチルアセトアミドを加熱あるいは溶媒浸漬によって脱離させることができ、脱離前後の物質の元素分析、吸収スペクトル測定、EXAFS 測定、放射光を用いた粉末 X 線回折測定等によって、脱離に伴って大きな構造変化を起こしていることを明らかにした。また、分子の脱離と同時に一万倍もの電気伝導率の増加を見出した。同様の手法を異なる金属イオンについても行っており、金属イオンの種類による安定性の違いも明らかにしている。

以上の研究成果は、博士論文として相応しい新規性を有しており、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、瞿李元提出の博士論文は、博士 (理学) の学位論文として合格と認める。